Dynamical Model for Brillouin Scattering Near the Critical Point of a Fluid*

Raymond D. Mountain

Institute for Basic Standards, National Bureau of Standards, Washington, D.C. 20234

(July 28, 1969)

A dynamical model for density fluctuations in a one-component fluid near the critical point is proposed and compared with existing measurements in carbon dioxide. The model is described by a set of linearized hydrodynamic equations modified to include a nonlocal pressure density relationship and to include relaxation in the volume viscosity. Parameters for the model are found which are consistent with bulk measurements. With these parameters the model reproduces, within experimental uncertainty, the observed Brillouin spectrum of critical opalescence in CO_2. The low frequency volume viscosity is found to diverge as the $-1/3$ power of $T - T_c$. An additional modification of the hydrodynamic equations, a frequency dependent thermal conductivity, is considered, but no definite conclusions can be reached as the Brillouin line-width data lack sufficient precision.

Key words: Brillouin scattering; critical opalescence; critical phenomena; density fluctuations in fluids; light scattering; volume viscosity.

1. Introduction

The dynamical structure of density fluctuations in a fluid is directly related to the spectral structure of light scattered by the density fluctuations. This structure has been the subject of a large number of theoretical [1][1] and experimental [2–4] papers. It has been established that the linearized hydrodynamic equations, suitably modified to include internal degrees of freedom, represent a satisfactory model for the dynamics of the long wave length density fluctuations in many simple fluids.

In this paper we propose to compare a model for the dynamics of density fluctuations in a one-component fluid near the critical point with recent experimental observations of the spectral structure of critical opalescence. The intent is to determine the main features of a model for critical fluctuations. We are not so much concerned with the precise values of parameters occuring in the model as we are that these parameters be in agreement with the known properties of the fluid system. The measurements are for carbon dioxide at the critical density for temperatures greater than the critical temperature. Three modifications of the linearized hydrodynamic equations will be examined. The first modification is the introduction of a nonlocal relationship between density and pressure fluctuations [5]. The second is the introduction of a frequency dependent volume viscosity and the third

modification is the introduction of a frequency dependent thermal conductivity [6, 7]. For convenience we assume the single relaxation time form for the frequency dependence of the volume viscosity and the thermal conductivity. Given the model and the experimental results currently available we conclude that the first and second modifications in the hydrodynamic equations are required. It is not possible to decide whether or not the thermal conductivity is frequency dependent.

2. Dynamical Model

Before we introduce the model for the density fluctuations in terms of a set of linearized hydrodynamic equations let us briefly state what is found experimentally. The spectrum consists of an intense central component and two relatively weak Brillouin components. The width of the central component may be expressed (in units of rad/sec) as

$$\Gamma_c = \chi k^2 [1 + \xi^2 k^2] \qquad (1)$$

where $\chi = \lambda / \rho_0 C_p$ is the thermal diffusivity at constant pressure. Here λ is the thermal conductivity, C_p is the specific heat at constant pressure and ρ_0 is the number density. The wave vector of the fluctuation is k. For the experiments to be considered $k = 2.18 \times 10^7$ m^{-1}. The temperature dependence of χ is found to be, for CO_2 above the critical point, proportional to $|T - T_c|^{-0.73 \pm 0.02}$ where T_c is the critical temperature ($T_c \simeq 303.2$ K for CO_2). Swinney and Cummins found

$\xi = (2.4 \pm 0.51) \times 10^{-9}/|T-T_c|^{2/3}$ m for CO_2 at the critical density [4].

The Brillouin components exhibit a large dispersion in the frequency shift $\omega_B = v_B k$; that is, $v_B > C_0$ the adiabatic sound speed. At the same time the width of the Brillouin components is appreciably greater than the width predicted by the unmodified hydrodynamic equations [2, 3].

Finally, the ratio of the intensity of the central component to the intensity of the Brillouin components is found to be proportional to $|T-T_c|^{-1.02 \pm 0.03}$ [2, 3].

The dynamical model for density fluctuations of wave vector k is

$$\frac{\partial \rho_k(t)}{\partial t} + \rho_0 \psi_k(t) = 0 \qquad (2)$$

$$\frac{\partial \psi_k(t)}{\partial t} = \frac{C_0^2 k^2}{\rho_0 \gamma} (1 + k^2/\kappa^2)\rho_k(t) + \frac{C_0^2 \beta_T}{\gamma} k^2 T_k(t)$$

$$- b_0 k^2 \psi_k(t) - k^2 \int_0^t b(t')\psi_k(t-t')dt', \qquad (3)$$

$$-\frac{C_v(\gamma-1)}{\beta_T} \frac{\partial \rho_k(t)}{\partial t} + \rho_0 C_v \frac{\partial T_k(t)}{\partial t} = -\lambda_\infty k^2 T_k(t)$$

$$- k^2 \int_0^t \Lambda(t') T_k(t-t') dt'. \qquad (4)$$

Here $\rho_k(t)$ is the kth spatial Fourier component of the density given that at $t=0$ that component had the value ρ_k. $T_k(t)$ and $\psi_k(t) = ik \cdot v_k(t)$ are the corresponding Fourier components of the temperature and velocity field. In eq (4) the entropy has been replaced by the temperature and the density using local thermodynamic equilibrium arguments. The pressure term in eq (3) has been also replaced by the temperature and density using a nonlocal relationship between the pressure and the density. The Fixman modification [5] was used so that

$$p_k(t) = \frac{mC_0^2}{\gamma} (1 + k^2/\kappa^2)\rho_k(t) + \frac{mC_0^2 \beta_T \rho_0}{\gamma} T_k(t).$$

Here κ^{-1} is the two particle correlation length, ρ_0 is the equilibrium number density and m is the mass of a molecule. Other quantities are C_0, the low frequency, adiabatic sound speed, $\gamma = C_p/C_v$ is the ratio of the specific heat at constant pressure C_p to the specific heat at constant volume C_v and β_T is the isobaric thermal expansion coefficient. The nonrelaxing longitudinal kinematic viscosity is $b_0 = (4/3\eta_s + \eta_v)/m\rho_0$ where η_s is the shear viscosity and η_v is the frequency independent volume viscosity. The relaxing part of the volume viscosity is contained in the convolution. We assume

$$b(t) = (C_\infty^2 - C_0^2)\exp(-t/\tau). \qquad (5)$$

The time dependence of b is arbitrarily chosen to be an exponential decay. While there is no reason to expect this simple form, we shall see that the data are, at present, adequately represented using this form. The "high frequency" speed of sound is C_∞. Equation (5) is a frequently used form for relaxing viscosities.

In eq (4) λ_0 is the static thermal conductivity and the relaxing part is $\Lambda(t)$. Again we choose an exponential decay:

$$\overline{\tau}\Lambda(t) = (\lambda_\infty - \lambda_0)\exp(-t/\overline{\tau}). \qquad (6)$$

The high frequency thermal conductivity λ_∞ is probably equal to the thermal conductivity when $T - T_c > 20$ K. Except near the critical point the thermal conductivity is insensitive to small changes in the temperature[8]. The form for eq (6) was chosen on the supposition that only the critical anomaly in the thermal conductivity can exhibit relaxation. Again the factor $\exp[-t/\overline{\tau}]$ was chosen for simplicity.

The spectrum of light scattered by density fluctuations is specified by the correlation function $\langle \rho_k(\omega)\rho_{-k} \rangle$ where $\rho_k(\omega)$ is the Fourier transform of $\rho_k(t)$. We shall determine $\langle \rho_k(\omega)\rho_{-k} \rangle$ for the model by solving eqs (2)–(6) as an initial value problem for $\rho_k(t)$ given that $\rho_k(0) = \rho_k$. Put another way, we use the equations of motion (2)–(6) in lieu of the conditional probability which relates $\rho_k(t)$ to ρ_k. If desired, the ensemble average indicated by the angular brackets $\langle \ldots \rangle$ may be computed using an equilibrium ensemble. The initial value $\langle \rho_k \rho_{-k} \rangle$ is not of special interest here as the Fourier components are independent in this model. [If there were coupling between ρ_k and ρ_{k+q} the initial values would be important.] The reader is referred to reference [1] for more detailed discussion of these calculations.

Solution of the model is straightforward when the Laplace transform is employed. The transform of $\rho_k(t)$ is

$$\rho_k(z) = \int_0^\infty e^{-zt}\rho_k(t)dt \qquad (7)$$

with similar expressions for $T_k(z)$ and $\psi_k(z)$. With the assumption that $\langle \rho_k T_{-k} \rangle = \langle \rho_k \psi_{-k} \rangle = 0$ it follows that

$$\frac{\langle \rho_k(z)\rho_{-k} \rangle}{\langle |\rho_k|^2 \rangle} = \frac{F(z)}{G(z)} \qquad (8)$$

with

$$F(z) = z^2\left[1 + \frac{(a_\infty - a_0)k^2 \overline{\tau}}{1 + z\overline{\tau}}\right]$$

$$+ z\left[b_0 k^2 + a_0 k^2 + \frac{(C_\infty^2 - C_0^2)k^2 \tau}{1 + z\tau}\right.$$

$$+ \frac{(a_\infty - a_0)k^2 \overline{\tau}}{1 + z\overline{\tau}}\left(b_0 k^2 + \frac{(C_\infty^2 - C_0^2)k^2 \tau}{1 + z\tau}\right)\right] \qquad (9)$$

$$+ \left(1 - \frac{1}{\gamma}\right)C_0^2 k^2 + a_0 k^2\left(b_0 k^2 + \frac{(C_\infty^2 - C_0^2)k^2 \tau}{1 + z\tau}\right)$$

and

$$G(z) = z^3 \left[1 + \frac{(a_\infty - a_0)k^2\bar{\tau}}{1 + z\bar{\tau}} \right]$$

$$+ z^2 \left[a_0 k^2 + b_0 k^2 + \frac{(C_\infty^2 - C_0^2)k^2\tau}{1 + z\tau} \right.$$

$$+ \frac{(a_\infty - a_0)k^2\bar{\tau}}{1 + z\bar{\tau}} \left(b_0 k^2 + \frac{(C_\infty^2 - C_0^2)k^2\tau}{1 + z\tau} \right) \right]$$

$$+ z \left[a_0 b_0 k^4 + a_0 k^2 \frac{(C_\infty^2 - C_0^2)k^2\tau}{1 + z\tau} \right.$$

$$+ C_0^2 k^2 (1 + k^2/\kappa^2\gamma)$$

$$+ \frac{C_0^2 k^2}{\gamma} (1 + k^2/\kappa^2) \frac{(a_\infty - a_0)k^2\bar{\tau}}{1 + z\bar{\tau}} \right]$$

$$+ \frac{a_0 k^2}{\gamma} C_0^2 k^2 (1 + k^2/\kappa^2). \tag{10}$$

We have introduced the quantities $a_0 = \lambda_0/\rho_0 C_v$ and $a_\infty = \lambda_\infty/\rho_0 C_v$.

An exact expression for $\langle \rho_k(\omega)\rho_{-k} \rangle$ may be obtained from eq (8) by replacing z by $i\omega$ and taking $1/\pi$ times the real part of the resulting expression.

$$\pi \frac{\langle \rho_k(\omega)\rho_{-k} \rangle}{\langle |\rho_k|^2 \rangle} = \mathrm{Re}\, \frac{F(i\omega)}{G(i\omega)}. \tag{11}$$

When this is done we find

$$\pi \frac{\langle \rho_k(\omega)\rho_{-k} \rangle}{\langle |\rho_k|^2 \rangle} = \frac{F_1 G_1 + F_2 G_2}{(G_1)^2 + (G_2)^2} \tag{12}$$

where $F(i\omega) = F_1 + i F_2$ and $G(i\omega) = G_1 + i G_2$.

The explicit forms for F_1 etc. are

$$F_1(\omega) = -\omega^2 \left[1 + \frac{(a_\infty - a_0)k^2\bar{\tau}}{1 + \omega^2\bar{\tau}^2} - \frac{(C_\infty^2 - C_0^2)k^2\tau^2}{1 + \omega^2\tau^2} \right.$$

$$- \frac{(a_\infty - a_0)k^2\bar{\tau}}{1 + \omega^2\bar{\tau}^2} \left(\frac{(C_\infty^2 - C_0)k^2\tau(\tau + \bar{\tau})}{1 + \omega^2\tau^2} + b_0 k^2\bar{\tau} \right) \right]$$

$$+ \left(1 - \frac{1}{\gamma} \right) C_0^2 k^2 + a_0 k^2 \left(b_0 k^2 + \frac{(C_\infty^2 - C_0^2)k^2\tau}{1 + \omega^2\tau^2} \right), \tag{13}$$

$$F_2(\omega) = \omega^3 \frac{(a_\infty - a_0)k^2\bar{\tau}^2}{1 + \omega^2\bar{\tau}^2} \left[1 - \frac{(C_\infty^2 - C_0^2)k^2\tau^2}{1 + \omega^2\tau^2} \right]$$

$$+ \omega \left[b_0 k^2 + a_0 k^2 + \frac{(C_\infty^2 - C_0^2)k^2\tau}{1 + \omega^2\tau^2} \right.$$

$$+ \frac{(a_\infty - a_0)k^2\bar{\tau}}{1 + \omega^2\bar{\tau}^2} \left(b_0 k^2 + \frac{(C_\infty^2 - C_0^2)k^2\tau}{1 + \omega^2\tau^2} \right)$$

$$\left. - a_0 k^2 \frac{(C_\infty^2 - C_0^2)k^2\tau^2}{1 + \omega^2\tau^2} \right], \tag{14}$$

$$G_1(\omega) = -\omega^4 \left[\frac{(a_\infty - a_0)k^2\bar{\tau}^2}{1 + \omega^2\bar{\tau}^2} \left(1 - \frac{(C_\infty^2 - C_0^2)k^2\tau^2}{1 + \omega^2\tau^2} \right) \right]$$

$$- \omega^2 \left[a_0 k^2 + b_0 k^2 + \frac{(C_\infty^2 - C_0^2)k^2\tau}{1 + \omega^2\tau^2} \right.$$

$$+ \frac{(a_\infty - a_0)k^2\bar{\tau}}{1 + \omega^2\bar{\tau}^2} \left(b_0 k^2 + \frac{(C_\infty^2 - C_0^2)k^2\tau}{1 + \omega^2\tau^2} \right)$$

$$- a_0 k^2 \frac{(C_\infty^2 - C_0^2)k^2\tau^2}{1 + \omega^2\tau^2} - \frac{C_0^2 k^2}{\gamma} \left(1 + \frac{k^2}{\kappa^2} \right)$$

$$\left. \frac{(a_\infty - a_0)k^2\bar{\tau}^2}{1 + \omega^2\bar{\tau}^2} \right] + \frac{a_0 k^2}{\gamma} C_0^2 k^2 (1 + k^2/\kappa^2) \tag{15}$$

and

$$G_2(\omega) = -\omega^3 \left[1 + \frac{(a_\infty - a_0)k^2\bar{\tau})}{1 + \omega^2\bar{\tau}^2} - \frac{-(C_\infty^2 - C_0^2)k^2\tau^2}{1 + \omega^2\tau^2} \right.$$

$$\left. - \frac{(a_\infty - a_0)k^2\bar{\tau}}{1 + \omega^2\bar{\tau}^2} \left(b_0 k^2\bar{\tau} + \frac{(C_\infty^2 - C_0^2)k^2\tau(\tau + \bar{\tau})}{1 + \omega^2\tau^2} \right) \right]$$

$$+ \omega \left[a_0 b_0 k^4 + a_0 k^2 \frac{(C_\infty^2 - C_0^2)k^2\tau}{1 + \omega^2\tau^2} + C_0^2 k^2 \left(1 + \frac{k^2}{k^2\gamma} \right) \right.$$

$$\left. + \frac{C_0^2 k^2}{\gamma} \left(1 + \frac{k^2}{\kappa^2} \right) \frac{(a_\infty - a_0)k^2\bar{\tau}}{1 + \omega^2\bar{\tau}^2} \right]. \tag{16}$$

3. Comparison With Experiment

The frequency spectrum of density fluctuations for the model may be computed by evaluating eq (12) for various values of ω. To do this requires specified values for the parameters a_0, a_∞, b_0, C_0, C_∞, γ, κ, τ, $\bar{\tau}$, and k. The wave vector k is determined by the experimental configuration. In what follows we shall use $k = 2.18 \times 10^7 m^{-1}$, the value appropriate to the measurements of Ford, Langley, and Puglielli [3]. It is possible to make reasonable estimates for a_∞, b_0, C_0, and C_∞ using various experimental results. We can also specify a_0/γ reliably. The remaining parameters κ, τ, $\bar{\tau}$ and γ are to be determined by requiring $\langle \rho_k(\omega)\rho_{-k} \rangle$ to correspond to the spectrum observed for CO_2.

First let us specify a_∞ and b_0. The critical anamoly in the thermal conductivity may be detected 40 K above the critical point in CO_2. However, most of the increase occurs for $|T - T_c| < 20$ K so a_∞ was chosen to be $1 \times 10^{-7} m^2/s$ which is comparable to a_0 at $T - T_c = 20$ K [8]. The shear viscosity and the nonrelaxing part of the volume viscosity are contained in b_0. A value $1.5 \times 10^{-7} m^2/s$ was chosen by assuming $\eta_v \approx \eta_s$ and using measured values for η_s [9].

The low frequency sound speed values C_0 were taken from figure 2 of reference [2]. These values correspond to the thermodynamic sound speed corrected for the vibrational degrees of freedom which are "frozen out" at the Brillouin frequency. This is the only place where the vibrational degrees of freedom are expected to be significant. Near the critical point the configurational contribution to the specific heat is large compared to the vibrational contribution so γ, the ratio of the specific heats, is not expected to depend significantly on the vibrational specific heat. The high frequency

sound speed values C_∞ were assumed to be slightly larger than the speeds obtained from figure 3 of reference [3]. For $T - T_c < 1$ K, $C_\infty = 194$ m/s was found to yield good agreement with experiment. Values of C_∞ for $T - T_c > 1$ K are shown in table 1.

The other quantity which may be specified is $a_0/\gamma = \lambda_0/\rho_0 C_p$ the thermal diffusivity at constant pressure. The width of the central component is, to lowest order in k^2, given by $\lambda_0 k^2/\rho_0 C_p$ (see eq (1)). The k^4 terms of this model may be found by seeking small solutions to the dispersion equation

$$G(z) = 0; \tag{17}$$

$G(z)$ is given in eq (10). The small z solution to eq (17) is

$$z \simeq -\frac{a_0 k^2}{\gamma}\left[1 + k^2/k^2 - a_0 k^2 \tau\left(\frac{C_\infty^2}{C_0^2} - 1\right) - \frac{a_\infty k^2 \bar{\bar{\tau}}}{\gamma}\right]. \tag{18}$$

Terms which are of order $1/\gamma$ compared to the retained terms have been dropped. Comparison with eq (1) indicates that

$$\xi^2 = \frac{1}{\kappa^2} - a_0 \tau\left(\frac{C_\infty^2}{C_0^2} - 1\right) - \frac{a_\infty \tau}{\gamma}. \tag{19}$$

Swinney and Cummins have determined a_0/γ by measuring the width of the central component in CO_2 and extracting the k^2 coefficient from those measurements [4].

The remaining parameters were evaluated as follows. An initial value was assumed for γ. [Once γ is specified, a_0 is obtained from the data of ref. 4]. The viscosity relaxation time τ was adjusted so that the Brillouin line width Γ_B, as determined from the spectrum obtained by evaluating eq (12), was in agreement with experiment. The sound speed $v(k)$ is not very sensitive to the value of τ as $\omega_B \tau = v(k) k \tau > 3$. Next the values of κ and $\bar{\bar{\tau}}$ were adjusted so that the central component line width is reasonable. In practice "reasonable" means ξ^2 nonnegative. The intensity ratio was then checked for overall consistency. Then a new value of γ was chosen and the process was

repeated until satisfactory agreement with experiment was achieved. No attempt to specify uncertainties in the parameters was undertaken. The final choice of values for τ, γ, κ, and $\bar{\bar{\tau}}$ is listed in table 2.

In determining γ and κ we are guided by the expectation that these quantities would be proportional to some power of $T - T_c$; namely [10],

$$\kappa = A(T - T_c)^\nu \tag{20}$$

and

$$\gamma = B(T - T_c)^{-\gamma + \alpha}. \tag{21}$$

The use of γ in eq (21) follows standard notation for exponents. Although this double meaning for γ is potentially confusing it should be clear from the context whether the exponent γ or $\gamma = C_p/C_v$ is intended. The exponents ν, γ and α specify the temperature dependence of the correlation length κ^{-1}, the specific heat at constant pressure C_p and the specific heat at constant volume C_v respectively. In the interval 0.05 K $\leqslant T - T_c \leqslant 5$ K we obtain agreement with the experimental data using $\nu \simeq 0.64$, $A = 1.6 \times 10^8 m^{-1}$, $\gamma - \alpha \simeq 1.1$ and $B = 129$.

The correlation length exponent $\nu \simeq 0.64$ is consistent with other estimates [11]. There have been no direct determinations of κ for CO_2 so it is not known whether or not $A = 1.6 \times 10^8 m^{-1}$ is a reasonable choice. An independent determination of κ by measuring the intensity of the scattered light as a function of wave vector (scattering angle) is needed.

The specific heat ratio exponent $\gamma - \alpha \simeq 1.1$ is just barely in agreement with the exponents γ and α determined from equation of state data [12]. The coefficient $B = 129$ is to be compared with an "experimental" value of $\gamma \simeq 120$ for $T - T_c \simeq 1$ K. This number was obtained by subtracting out the vibrational contribution to the specific heat ratio obtained from equation of state data.

Although the Brillouin line-width data may be fit using a frequency dependent thermal conductivity, the data may also be fit using $\bar{\bar{\tau}}$, the thermal conductivity relaxation time, set equal to zero. For example a set of values for $\bar{\bar{\tau}}$ were obtained which may be represented as

$$\bar{\bar{\tau}} = 2 \times 10^{-11}(T - T_c)^{-1}\text{s} \tag{22}$$

in the interval 0.05 K $\leq T - T_c \leq 2$ K. This form has *no* significance as for $T - T_c = 0.05$ K, $\bar{\tau} = 5 \times 10^{-10}$s and $\tau = 0$ yield Brillouin line widths lying within the uncertainty of the measured value. Until more precise Brillouin line-width data become available it will not be possible to decide whether or not a frequency dependent thermal conductivity is an appropriate feature of a dynamical model of critical point density fluctuations.

The values for the relaxation time τ may be approximately represented as

$$\tau = 8 \times 10^{-10} |T - T_c|^{-1/3} s \qquad (23)$$

The value, $-1/3$, of the exponent in eq (23) is an unexpected result in that a $-1/3$ power divergence of the volume viscosity has not been suggested by theoretical attempts to determine transport coefficients in the critical region [6, 7].

Two other sets of parameters were considered. The first of these had the specific heat ratio exponent $\gamma - \alpha = 1$. While an acceptable fit to the experimental data was obtained, this set of parameters was rejected because $\gamma - \alpha = 1$ is not consistent with γ and α determined from equation of state data. The second set of parameters had $\gamma - \alpha = 1.2$. It was not possible to fit the intensity ratio data with the second set.
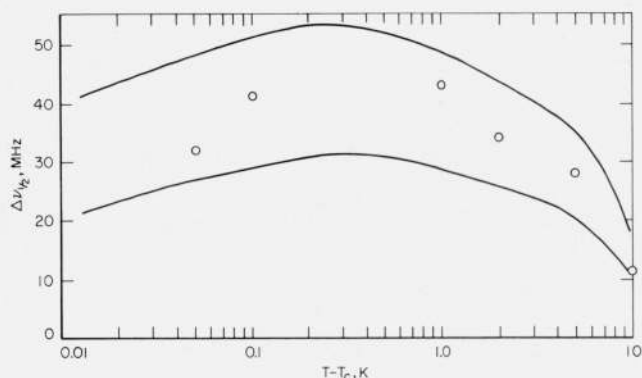

FIGURE 1. *Comparison of experimental and computed Brillouin line widths.*

The circles are the computed line widths. The solid lines indicate the uncertainty in the experimental results. This includes both the quoted uncertainty and the spread of the data in figure 3 of reference [3].

The type of fit obtained for the Brillouin line width is shown in figure 1 and for the intensity ratio as shown in figure 2. The error band in figure 1 is taken from reference [3] and represents experimental uncertainty and spread in the data. No uncertainty for the intensity ratio is quoted in reference [3], but the scatter in the data is such that our computed values are compatable with the experimental values. The central component line widths are not indicated as the computed values were required to agree with the experimental widths.

4. Discussion

It is not reasonable to expect the single relaxation time model for the volume viscosity to provide an
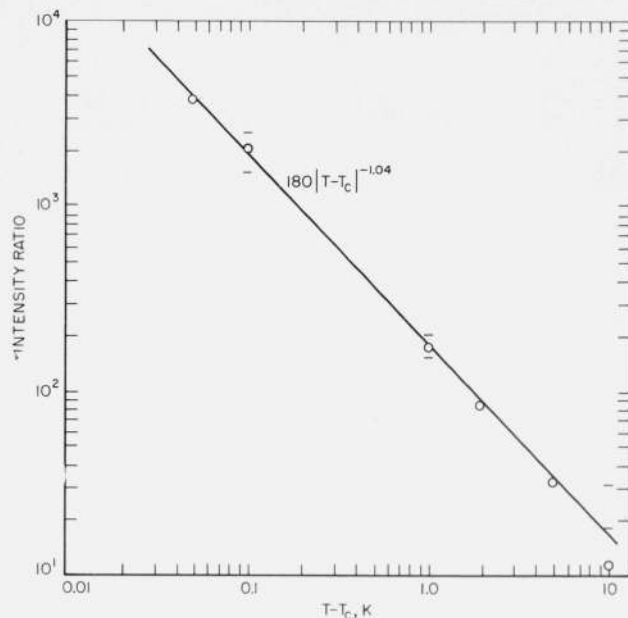

FIGURE 2. *Comparison of experimental and computed intensity ratios.*

The solid circles are computed values; the error bars indicate the spread of the experimental points in figure 3 of reference [3]. The solid line, $180|T - T_c|^{-1.04}$, was drawn through the computed points "by eye". It is, on this plot, indistinguishable from $185|T - T_c|^{-1.02}$ which is the least squares fit to the experimental points.

adequate description of density fluctuations in the critical region. More probably a model with a "distribution of relaxation times" will be found when improved data become available, to yield a better description [13]. This would require a modification of eq (5) with corresponding changes in eqs (9), (10), (13), (14), (15), and (16).

A fairly good test of the single relaxation time model can be made by measuring the Brillouin sound speed as a function of wave vector. With a single relaxation time the dispersion in v_B, the Brillouin speed, occurs over a fairly narrow range in k. With a distribution of times the range in k over which dispersion in v_B is exhibited increases and the increase in v_B with increasing k is less abrupt. We have determined v_B as a function of k using the parameters in tables 1 and 2. These speeds are plotted in figure 3 as functions of $T - T_c$ for four different values of the wave vector k. The limiting curves for C_∞ and C_0 are also shown. The minimum in v_B is due to the decrease in C_0 as $T \to T_c$. The wave vector dependence is shown in figure 4. There $(v_B/C_0)^2$ for different $T - T_c$ is plotted as a function of k. If a "distribution of relaxation times" model were used, the slope of the curves in figure 4 would be less steep.

A dynamical model for long wavelength density fluctuations in a fluid near the critical point has been described by the linearized hydrodynamic equations which were modified to allow for nonlocal pressure-density relationship and to allow for frequency dependence in the volume viscosity. The parameters of this model may be chosen so that the calculated spectrum is in agreement with the observed spectrum. The
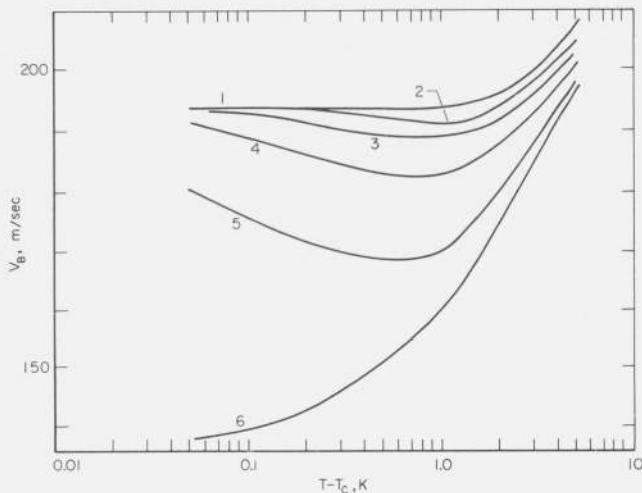
FIGURE 3. *The Brillouin speed* v_B *versus* $T - T_c$ *for several values of wavevector.*

Curve 1, C_∞; curve 2, $k = 2.18 \times 10^{-7} \mathrm{m}^{-1}$ ($\theta = 166°$) curve 3, $k = 1.54 \times 10^7 \mathrm{m}^{-1}$ ($\theta = 90°$); curve 4, $k = 1 \times 10^7 \mathrm{m}^{-1}$ ($\theta = 54°$); curve 5, $k = 5 \times 10^6 \mathrm{m}^{-1}$ ($\theta = 26°$); curve 6, C_0.
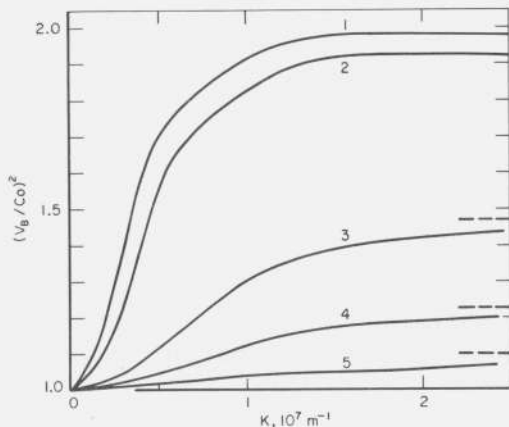

FIGURE 4. *The dispersion in the Brillouin speed as a function of wavevector is indicated as* $(v_B/C_0)^2$ *versus* k *for several values of* $T - T_c$.

Curve 1, $T - t_c = 0.05$ K; curve 2, $T - T_c = 0.1$ K; curve 3, $T - T_c = 1$ K; curve 4, $T - T_c = 2$ K; curve 5, $T - T_c = 5$ K. The limiting values $(C_\infty/C_0)^2$ are shown as horizontal lines for curves 3, 4, and 5.

parameters are *consistent* with other measurements although this could change as more precise measurements are made.

Two comments are in order. The first is that near the critical point, the intensity ratio is *not* a measure of the ratio of the specific heats. As shown in figure 2, calculated values of the intensity ratio are described by

$$\frac{I_c}{2I_B} = 180|T - T_c|^{-1.04}.$$

To obtain this set of values we used

$$\gamma = 129|T - T_c|^{-1.1}.$$

Obviously $I_c/2I_B \neq \gamma - 1$. The intensity ratio measures not only γ but also $(v_B k\tau)^2$. Unfortunately neither of

these quantities enters in a very simple way. Nevertheless the intensity provides an important overall consistency check on the parameters of the model.

The second comment is that the k^4 term in the central component line width is not simply a measure of the two particle correlation length. This is seen clearly in eq (19).

A more careful evaluation of the model could be made if two sets of measurements were to be performed. The correlation length, κ^{-1}, has been used as an adjustable parameter. It should be determined from other light scattering measurements [14].

The values of κ used in this paper imply a considerable angular dissymmetry in the intensity of the scattered light for $T - T_c < 0.1$ K. This is just the region where multiple scattering becomes important so it is not possible to say if our values of κ are consistent with the measurements discussed in reference [14]. The uncertainty in the Brillouin line width measurements is too large to permit any meaningful evaluation of the frequency dependence of the thermal conductivity. The line width measurements should be made with greater precision.

5. References

[1] No attempt to provide a complete set of references will be made. Some relevant papers are: 1a, 1b, 1c.
    1a. Mountain, R. D., J. Res. Nat. Bur. Stand. (U.S.) **70A** (3) 207–220 (1966).
    1b. Nichols, W. H., and Carome, E. F., J. Chem. Phys. **49**, 1000 (1968).
    1c. Bhatia, A. B., and Tong, E., Phys. Rev. **173**, 231 (1968).
[2] Gammon, R. W., Swinney, H. L., and Cummins, H. Z., Phys. Rev. Letters **19**, 1467 (1967).
[3] Ford, N. C., Jr., Langley, K. H., and Puglielli, V. G., Phys. Rev. Letters **21**, 9 (1968).
[4] Swinney, H. L., and Cummins, H. Z., Phys. Rev. **171**, 152 (1968).
[5] Fixman, M., J. Chem. Phys. **33**, 1357 (1960). The effects of only this modification have been examined by H. Z. Cummins and H. L. Swinney, J. Chem. Phys. **45**, 4438 (1966). See also M. Sh. Giterman and V. M. Kontorovich, Sov. Phys. JETP **20**, 1433 (1965).
[6] Kadanoff, L. P., and Swift, J., Phys. Rev. **166**, 89 (1968).
[7] Kawasaki, K., Prog. Theoret. Phys. **40**, 930 (1968).
[8] Green, M. S., and Sengers, J. V., eds., National Bur. Std. (U.S.) Misc. Publ. No. 273 (1966); J. V. Sengers, p. 165.
[9] Kestin, J., Whitelaw, J. H., and Zien, T. F., Physica **30**, 161 (1964).
[10] Fisher, M. E., p. 21 of ref. 8.
[11] Kadanoff, L. P., Gotze, W., Hamblen, D., Hecht, R., Lewis, E. A. S., Palciauskas, V. V., Rayl, M., and Swift, J., Rev. Mod. Phys. **39**, 395 (1967); M. E. Fisher, Rept. Progr. Phys. **30**, 615 (1967); P. Heller, *Ibid.*, 731.
[12] Vicentini-Missoni, M., Levelt-Sengers, J. M. H., and Green, M. S., Phys. Rev. Letters **22**, 389 (1969). They find 1.1 $< \gamma - \alpha < 1.22$.
[13] Chynoweth, A. G., and Schneider, W. G., J. Chem. Phys. **20**, 1777 (1952).
[14] McIntyre, D., and Sengers, J. V., in Physics of Simple Liquids, eds., H. N. V. Temperly, J. S. Rowlinson and G. S. Ruchbrooke (North-Holland Publishing Co., Amsterdam, 1969) pp. 470–471.